(12) UK Patent Application (19) GB (11) 2 048 229 A

(21) Application No 8012758
(22) Date of filing 17 Apr 1980
(30) Priority data
(31) 31957U
(32) 20 Apr 1979
(31) 32095U
(32) 20 Apr 1979
(33) United States of America (US)
(43) Application published 10 Dec 1980
(51) INT CL³ C01F 7/48 A61K 7/32
(52) Domestic classification C1A 530 D30 G4 G4D30 PB5 A5B FG
(56) Documents cited GB 1568831 GB 2027419A GB 1460966 GB 1353916
(58) Field of search C1A
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(54) Aluminium Chlorhydroxide and Preparation Thereof

(57) A novel aluminium chlorhydroxide comprises at least 45% by weight of an $Al^{c'}$ group of aluminium chlorhydroxide complexes which are characterised by exhibiting anomalous permeation and reaction rates in gel permeation chromatography and ferron tests. This aluminium chlorhydroxide is prepared by ageing aluminium chlorhydroxide in an aqueous medium.

The product is used in anti-perspirant compositions.

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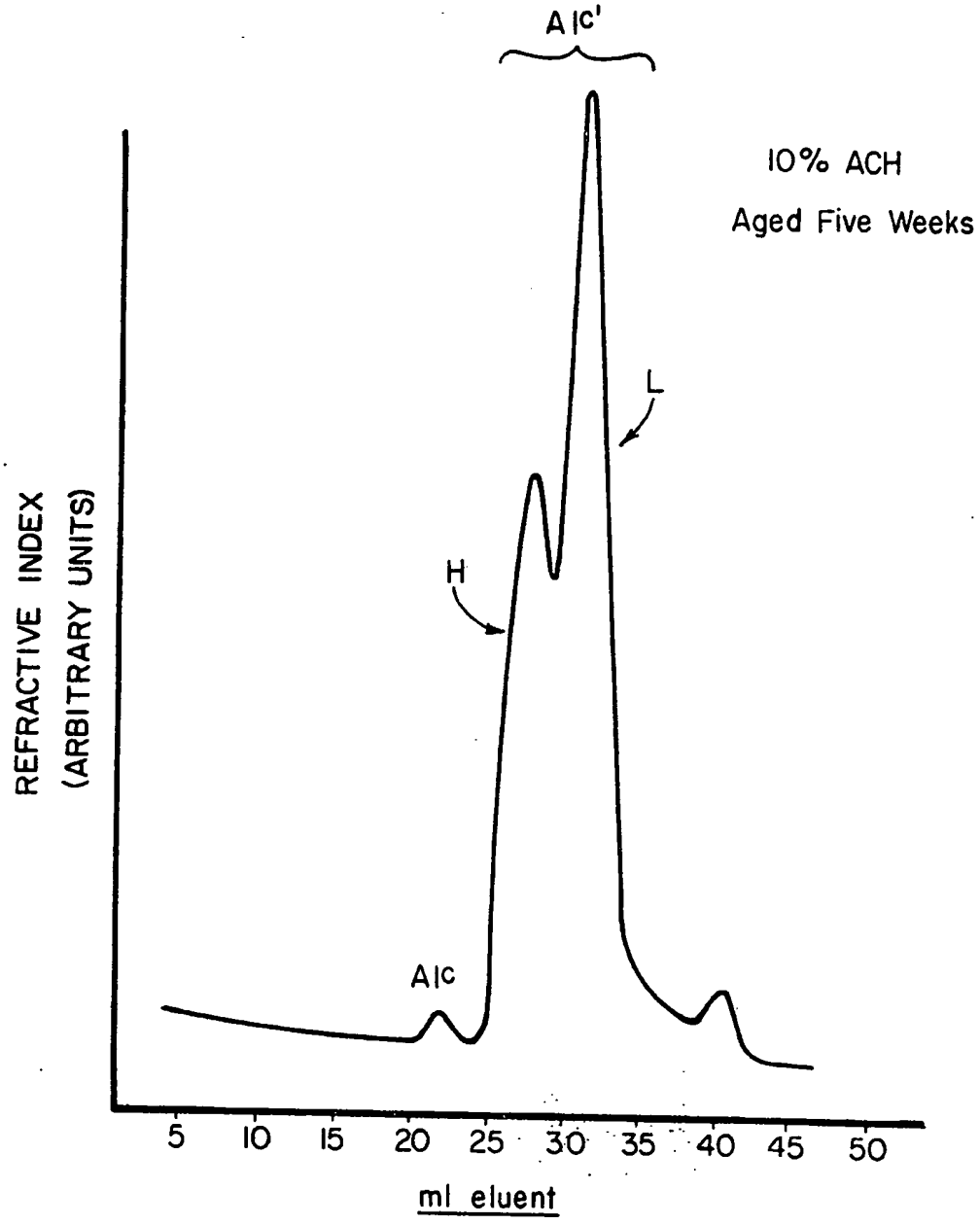
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Fig. 1

SPECIFICATION

Aluminium Chlorhydroxide and Preparation Thereof

Aluminium chlorhydroxides have long been used as antiperspirants. In general, such chlorhydroxides are, in the presence of water, complexes made up of mixtures of polymeric species of various sizes and molecular structures. The aluminium chlorhydroxides which have been found most useful as antiperspirants may be represented by the empirical formula:

$$Al_2(OH)_5Cl$$

In the past, aluminium hydroxyl polymers which are related to such aluminium chlorhydroxides have been shown to be made up of three broad basic groups by spectrophotometrically following their complexing rates with 8-hydroxy-7-iodo-5-quinoline-sulphonic acid (ferron). Such basic groups have been referred to as Al^a, Al^b and Al^c. The first group, Al^a, has the fastest complexing rate (almost instantaneous); the Al^b group has an intermediate complexing rate (the reaction is complete in about an hour); and the Al^c group has the slowest rate (generally the reaction takes a matter of days). It is known that aluminium chlorhydroxides exhibit a similar phenomenon when reacted with ferron. For convenience, the fastest reacting group within the aluminium chlorhydroxide complexes may be referred to as Al^a, the intermediate reacting group as Al^b, and the slowest group as Al^c. It is also known that when aqueous solutions of aluminium chlorhydroxides are subjected to gel permeation chromatography, the three groups exhibit different retention times. The Al^a group has the longest retention time which is indicative that it is made up of the lowest molecular size materials, the Al^b group has an intermediate retention time, indicating it comprises complexes of intermediate molecular size, and the Al^c group has the shortest retention time indicating that it is made up of the highest molecular size complexes.

We have now found that there is a further group of complexes within the aluminium chlorhydroxides which has not previously been identified or recognized and which is more efficacious as an antiperspirant than the known groups referred to above. This more efficacious group of complexes, which for convenience may be referred to as $Al^{c'}$, is present in amounts of from 10 to 30% by weight in aluminium chlorhydroxides presently available, although its presence has not been recognized or appreciated up to now. We have further found that aluminium chlorhydroxides can be modified or produced so as to contain a substantially higher amount of the $Al^{c'}$ group and the chlorhydroxides so modified or produced are novel compositions of matter. Generally, the aluminium chlorhydroxides of this invention are distinguished from known aluminium chlorhydroxides in that they contain at least 45% by weight, preferably 60% and more preferably at least 70%, of the $Al^{c'}$ group of complexes.

Even with the advanced analytical techniques available today, it is still not possible to determine the structure of aluminium chlorhydroxide complexes. Accordingly, in defining the newly discovered $Al^{c'}$ group of complexes, it is necessary to resort to empirical procedures. Broadly, the new $Al^{c'}$ complex can be defined by its diffusion constant in gel permeation chromatography and its complexing rate in the ferron test. Using such criteria, the $Al^{c'}$ group of complexes can be broadly characterised by having a diffusion constant in gel permeation chromatography which is within that range generally found for the Al^b group of complexes and a complexing rate in the ferron test in the range found for the Al^c complexes. Such anomalous results clearly indicate that the complexes within the $Al^{c'}$ group have a distinct structure not heretofore recognized or appreciated.

According to the present invention, therefore, there is provided an aluminium chlorhydroxide comprising at least 45% by weight, preferably at least 60% by weight, and more preferably at least 70% by weight, of an $Al^{c'}$ group of aluminium chlorhydroxide complexes which are characterised by exhibiting anomalous permeation and reaction rates in gel permeation chromatography and ferron tests.

The term "$Al^{c'}$" will hereinafter be used to refer to that group of aluminium chlorhydroxide complexes which are more efficacious as antiperspirants and exhibit anomalous results in gel permeation chromatography and the ferron reaction.

Generally, the diffusion rates in gel permeation chromatography and the reaction rates in the ferron complexing test will vary with the conditions under which such procedures are conducted. Accordingly, in order to more specifically define the $Al^{c'}$ group of complexes, it is desirable to specify the conditions under which such procedures are conducted.

Generally, the $Al^{c'}$ group of complexes can be said to have a diffusion constant in gel permeation chromatography of from 0.1 to 0.7, preferably from 0.2 to 0.65, and more preferably from 0.3 to 0.55 when such permeation is carried out under the following conditions:

Eluent—0.1N KCl
Concentration of aluminium chlorhydroxide—10% by weight
Temperature—Room Temperature
Type of gel material—Em Gel PGM-2000 (Trade name of E. Merck Co. for a polyethylene glycol dimethacrylate type gel.)

In the ferron test, the $Al^{c\prime}$ group of complexes requires a minimum of about 3 days for the reaction to go to completion under the following conditions:

Reaction medium—Water
Conc. of ferron—2.8×10^{-3} M
Conc. of aluminium chlorhydroxide—2.3×10^{-4} M
Temperature—Room Temperature
pH—5
Buffer—Hydroxylamine hydrochloride, hydrochloric acid and sodium acetate.

At least in aluminium chlorhydroxides which have a pH of 4.0 to 4.7, for example $Al_2(OH)_5Cl$, the $Al^{c\prime}$ group of complexes can be further characterised by the fact that in gel permeation chromatography (using an Em Gel) they produce a doublet within the peak in which they fall (for example, between diffusion constants 0.3 to 0.55). The single Figure of the accompanying drawing is a chromatogram of an aluminium chlorhydroxide within the scope of the present invention which was run using an Em Gel PGM-2000. The two peaks of the doublet have been found to be distinct fractions and the first peak, presumably comprising the larger molecules of the two fractions, has been called H and the second L. Such fractions may also be referred to as $Al_H^{c\prime}$ and $Al_L^{c\prime}$.

The $Al^{c\prime}$ group of complexes of this invention can be still further characterized by the fact that the molecules making up the group are less than 100Å in size in aqueous solutions.

For the purpose of this invention, the percent of the $Al^{c\prime}$ group in an aluminium chlorhydroxide is determined by assuming that the Al^{c} group of complexes plus the $Al^{c\prime}$ group of complexes is about 90% by weight of the aluminium chlorhydroxide and then multiplying 90% by the ratio of the height of the $Al^{c\prime}$ peak to the combined heights of the Al^{c} and $Al^{c\prime}$ peaks on a gel chromatogram such as shown in the accompanying drawing, i.e.

$$\%Al^{c\prime} = \frac{Al^{c\prime}}{Al^{c}+Al^{c\prime}} \times 90\%$$

The novel aluminium chlorhydroxide of this invention may be prepared by ageing the aluminium chlorhydroxide presently available (that is, those containing less than 30% of the $Al^{c\prime}$ group) in an aqueous medium until the aluminium chlorhydroxide contains at least 45% of the $Al^{c\prime}$ group as determined by the peak height ratio. In carrying out the ageing process, it has generally been found that the reaction is temperature, concentration and time dependent. In general, the ageing should be carried out at temperatures below 100°C, preferably at 90°C or lower and more preferably at about 80°C or lower. Generally there is no lower limit on the ageing temperature, but when the ageing is carried out at room temperature or lower the reaction rate is considerably slower, for example a 10% by weight solution at room temperature takes about five weeks. It is preferable that the ageing be carried out at a temperature above 50°C. As to the concentration, it has generally been found that the concentration should be at least 5% by weight, preferably at least 7.5% and more preferably 10% or more. As to the upper limit on concentration, it is generally less than 40% by weight, preferably less than 35% by weight and more preferably less than 30%. At between 27.5 and 7.5% and more particularly between 25% and 10% especially good results were obtained. Within the temperature and concentration ranges specified above, the reaction rate of the ageing process will generally increase as the temperature is raised and decrease when the concentration is increased. The effect of concentration and temperature on the reaction is illustrated in Table I below:

Table I

Time Required to Produce Aluminium Chlorhydroxides (ACH) which contain at least 70% $Al^{c\prime}$

	Temperature °C		
ACH Concentration	*50°*	*65°*	*80°*
10%	1 week	1 day	8 hours
15%	——	4 days	16 hours
25%	——	3 weeks	1 week

Generally the conditions which are most conducive for producing the aluminium chlorhydroxides of this invention will promote the depolymerization of the larger size polymeric molecules and the overall composition of the resulting product in water will generally be substantially free, i.e. contain less than 2% by weight, of molecules greater than 100Å in size.

After the aluminium chlorhydroxides of this invention have been produced by the ageing process described above, the reaction solution may be concentrated by distillation. Such distillation is preferably carried out at a temperature below 100°C and more preferably below about 80°C and at reduced pressure, so as not to convert the aluminium chlorhydroxide to aluminium oxide. Particularly good results are obtained by carrying out the concentration step at 34°C to 38°C and 28 mmHg pressure. As the concentration of aluminium chlorhydroxides increases by removal of water during the

distillation, the concentration of the $Al^{c'}$ group is believed to start to gradually decrease as the overall concentration of the aluminium chlorhydroxide begins to exceed about 30%. Thus, although it is possible to produce 50% solutions by distillation, such solutions are not stable for extended periods and the amount of the $Al^{c'}$ present will gradually decrease until the amount present is below that specified for the aluminium chlorhydroxide of this invention. In light of such instability at higher concentrations, it has been found that if the aluminium chlorhydroxides are going to be used in water-based antiperspirant compositions, they should be concentrated to a range of from 10% to 30% in which they will generally remain stable. If it is desired to produce the aluminium chlorhydroxide as a powder, the reaction solutions may be concentrated, for example up to about 50%, and they should then be converted to the powder shortly thereafter, for example within 24 hours, under conditions in which the decrease of the $Al^{c'}$ group does not take place to any great extent. One such method is to rapidly convert the concentrated solution to a powder, for example by spray drying. Spray drying has been successfully carried out at an inlet temperature of 150°C and an outlet temperature of 75 to 80° and a feed rate of 280 ml per minute. Another method is to convert the concentrated solution to a powder under conditions in which the decrease of the $Al^{c'}$ group will take place very gradually, for example freeze drying. Freeze drying has been successfully carried out at −40°C and a pressure of 1 mm Hg. In drying the aqueous solution to powder, care should be taken not to remove all the bound water because as is known such total removal generally irreversibly destroys the antiperspirant activity of the material. The dried powder should preferably contain 3 to 20% by weight and more preferably 3 to 15% by weight of bound water. In powdered form the aluminium chlorhydroxides of this invention are quite stable.

The aluminium chlorhydroxides of this invention may be used as antiperspirants in the various forms well known to the art, for example solutions, creams, lotions, sticks, roll-ons, pads and aerosols. When they are used in water-based compositions or in water-alcohol based compositions, the amount of water present should preferably be such that the concentration of the aluminium chlorhydroxide in the water alone, that is exclusive of all other liquids present, is from 5 to 30% by weight, in which range the $Al^{c'}$ group is generally stable. The especially preferred concentration is from 7.5% to 27.5%.

When the aluminium chlorhydroxides of this invention are to be used as powders in substantially anhydrous systems, it will not usually be necessary to use any special precautions because as pointed out above, they are quite stable in this form. The aluminium chlorhydroxides of this invention are especially useful in anhydrous suspension-type systems well known to the art, such as roll-ons and pump and aerosol sprays, in which the powders are suspended in hydrophobic vehicles, such as isopropyl myristate, volatile cyclic silicones, and mixtures thereof. Such systems usually also comprise a suspending agent, such as a hydrophobic bentonite, for example Bentone 34 and 38, and silica, for example Cab-O-Sil M5. When the suspensions are used in aerosol form they will also include well known propellants, such as the hydrocarbons and the halocarbons.

Unlike the presently available aluminium chlorhydroxides, the efficacy of the aluminium chlorhydroxides of this invention is concentration dependent. This can be quite advantageous in that, within limits, one may formulate antiperspirant compositions to provide a desired level of efficacy by merely varying the amount of active material present. In aqueous systems, the improved efficacy of the aluminium chlorhydroxides of this invention generally become more apparent and significant when they are used in amounts above 15%, for example 20% by weight. In such aqueous systems at concentrations of 20% or more the aluminium chlorhydroxides of this invention have been found to be at least 20% more efficacious than the aluminium chlorhydroxides presently available.

In order that the invention may be more fully understood, the following examples are given by way of illustration only.

Example I

A 10% aqueous solution of aluminium chlorhydroxide was aged at 50°C for five weeks. The resulting aluminium chlorhydroxide composition which contained about 90% of the $Al^{c'}$ group was freeze dried to a powder in a laboratory freeze drier at about 5 mm Hg. The powder (ACH'), together with a control of standard aluminium chlorhydroxide (ACH), was formulated into water-based antiperspirant compositions containing 10, 15 and 20% by weight, respectively, of the aluminium chlorhydroxides. The resulting compositions were tested for sweat reduction using a trade-recognized gravimetric procedure on thermally stimulated human subjects. The results are set forth in Table II below:

Table II

Relative Percent Sweat Reduction—90% Confidence Levels After Six Applications*

	Relative Percent Sweat Reduction	
Concentration	*ACH*	*ACH'*
10%	36.7	40.5
15%	37.8	41.8
20%	39.3	48.1

As can be noted, especially at the 20% level, the aluminium chlorhydroxides of this invention are significantly superior to the presently available aluminium chlorhydroxides.

* A number of applications of the product which the trade would recognize as being reflective of the typical efficacy of the antiperspirant.

Example II

300 gallons of a 10% by weight aqueous solution of a commercially available aluminium chlorhydroxide were aged at 80°C for 16 hours. At the end of the ageing period, a small aliquot of the composition was subjected to gel permeation chromotography. The chromotogram indicated that the aluminium chlorhydroxide present contained at least 90% of the $Al^{c'}$ group. About 10 Kg of the composition was freeze dried at −40°C and 1 mm Hg to provide about 1 Kg of powdered material. A chromatogram of a 10% aqueous solution of the freeze dried material was identical to that of the mother solution thus indicating that the aluminium chlorhydroxide of the invention is stable to freeze drying.

Example III

The aluminium chlorhydroxide powder produced in Example II (ACH') was ground and sieved, using a 230 mesh sieve, and were formulated into a suspension-type, substantially anhydrous, roll-on antiperspirant composition, together with a standard powdered ACH (control). The make-up of the formulations was as follows:

	Formulations (Percent by Weight)	
Ingredients	*ACH'*	*ACH (Control)*
ACH'	20.0	—
ACH	—	20.0
Volatile cyclic silicone	74.0	74.0
Bentone 38 (a hydrophobic quaternized bentonite clay)	3.50	3.50
Alcohol (200 proof)	2.31	2.31
Deionized water	0.19	0.19
	100%	100%

The resulting compositions were tested for sweat reduction using a trade-recognized gravimetric procedure on thermally stimulated human subjects. The ACH' composition was found to be significantly superior to the ACH (control) composition in reducing sweat.

Example IV

A 10% aqueous solution of a commercially available aluminium chlorhydroxide was aged as described in Example II and concentrated to about a 50% solution at a temperature of from 34°C to 38°C and a pressure of 28 mm Hg. The concentrated solution was spray dried at an inlet temperature of about 150°C, an outlet temperature of 75° to 80°C and a feed rate of about 280 ml per minute. When the resulting material was tested as an antiperspirant in a suspension-type composition similar to that of Example III, except that 25% of the material was used, it gave comparable results.

In the above Examples, the aluminium chlorhydroxide used had an empirical formula of about $Al_2(OH)_5Cl$.

Claims

1. An aluminium chlorhydroxide comprising at least 45% by weight of an $Al^{c'}$ group of aluminium chlorhydroxide complexes which are characterised by exhibiting anomalous permeation and reaction rates in gel permeation chromatography and ferron tests.

2. An aluminium chlorhydroxide according to claim 1, which contains at least 60% by weight of the $Al^{c'}$ group of complexes.

3. An aluminium chlorhydroxide according to claim 1, which contains at least 70% by weight of the $Al^{c'}$ group of complexes.

4. An aluminium chlorhydroxide according to any of claims 1 to 3, which is further characterised by forming a doublet in the chromatogram when it is subjected to gel permeation chromatography using a polyethylene glycol dimethacrylate gel.

5. An antiperspirant composition comprising an aluminium chlorhydroxide according to any of claims 1 to 4.

6. An antiperspirant composition according to claim 5, which is water-based and in which the concentration of the aluminium chlorhydroxide is from 5% to 30% by weight, based on the water content thereof.

7. An antiperspirant composition according to claim 6, in which the concentration is from 7.5% to 27.5% by weight.

8. An antiperspirant composition according to claim 5 which is substantially anhydrous and in which the aluminium chlorhydroxide is in powder form.

9. A process for producing an aluminium chlorhydroxide according to any of claims 1 to 4, which comprises ageing aluminium chlorhydroxide in an aqueous medium.

10. A process according to claim 9, in which the ageing is carried out at a concentration of from 5% to 40% by weight and at a temperature of from 50°C to 100°C.

11. A process according to claim 10, in which the concentration is from 5% to 30% by weight.

12. A process according to claim 10, in which the concentration is from 7.5% to 27.5% by weight.

13. A process according to any of claims 9 to 12, in which ageing is carried out at a temperature of from 50°C to 90°C.

14. A process according to any of claims 9 to 13, in which ageing is carried out at a temperature of from 50°C to 80°C.

15. A process according to any of claims 9 to 14, in which the resulting aqueous composition is spray dried to a powder.

16. A process according to any of claims 9 to 14, in which the resulting aqueous composition is freeze-dried to a powder.

17. An aluminium chlorhydroxide according to claim 1 substantially as herein described in any of the Examples.

18. An antiperspirant composition according to claim 5 substantially as hereindescribed in any of Examples I, III and IV.

19. A process for producing an aluminium chlorhydroxide according to claim 1 substantially as herein described in any of Examples I, II and IV.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.